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Solid State Thermochemical Decomposition of Neat 1,3,5,5-Tetranitrohexahydropyrimidine (DNNC) and Its DNNC-d₆ Perdeuterio-Labeled Analogue

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Abstract

The solid state exothermic thermochemical decomposition kinetics of neat 1,3,5,5-tetranitrohexahydro-pyrimidine (DNNC) and its perdeuterio DNNC-d₆ deuterium labeled analogue were obtained by isothermal differential scanning calorimetry (IDSC) at 142, 145, and 148 °C. Rate constants subjected to kinetic deuterium isotope effect (KDIE) criteria suggest that C-H bond rupture in either one or both types of the chemically inequivalent alternating -CH₂- methylene groups of the DNNC ring structure constitutes the exothermic rate-controlling step. An energy of activation equal to 115 kJ/mole was determined for the exothermic DNNC-d₆ decomposition, and from which 106 kJ/mol was calculated for unlabeled DNNC. The exothermic DNNC decomposition follows an extended endothermic induction period with a higher 128 kJ/mole activation energy during which a catalytic species may form by a different rate-limiting step prior to initiating the exothermic decomposition and resultant energy release.

Keywords: 1,3,5,5-Tetranitrohexahydropyrimidine, DNNC, Solid State Decomposition, Deuterium Isotope Effect

1 Introduction

The heterocyclic DNNC molecule is comprised of a unique hybrid chemical structure that incorporates features that define both high energy geminal dinitroalkane and cyclic nitramine compounds. As such, it contains two types of methylene groups (-CH₂-). One non-equivalent -CH₂- group is sandwiched between two N-NO₂ structural groups, and two chemically equivalent -CH₂- groups each flank the geminal -C(NO₂)₂- structural feature. First synthesized in 1982,^(2,3) this DNNC⁽⁴⁾ hybrid

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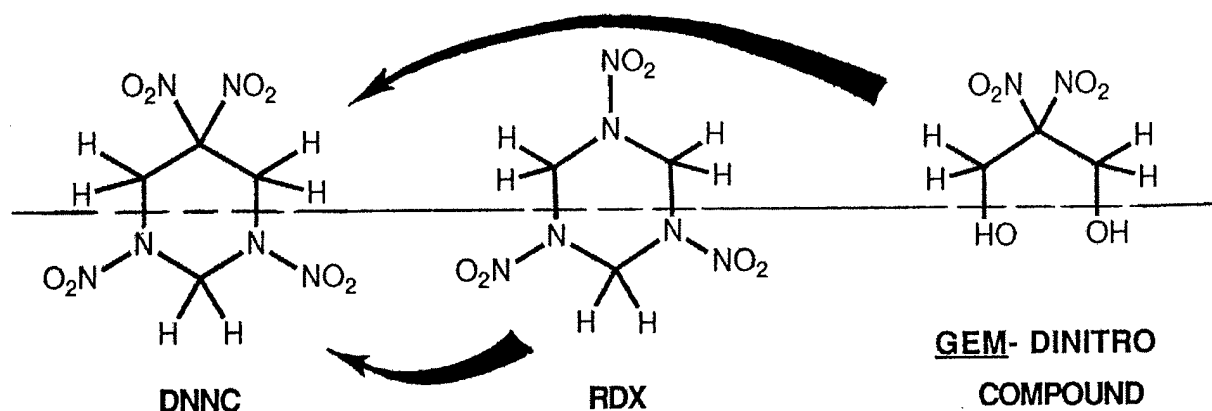


Figure 1. Intramolecular hybrid structure of the DNNC molecule.

structure provides a high energy pseudo-nitramine heterocycle with an impact sensitivity significantly lower than that exhibited by its structurally related six-membered cyclic RDX nitramine (Figure 1). The explosive initiation sensitivity of DNNC resembles that of the more stable nitroaromatic TNT molecule, but when initiated, its detonation energy output is significantly higher than TNT and rivals the RDX nitramine.⁽²⁾ Thus, the DNNC pseudo nitramine exhibits energy and sensitivity properties associated with both nitramine and nitroaromatic compounds.

The DNNC thermochemical stability also is similar to TNT.⁽⁵⁾ Like TNT, DNNC melts without noticeable or significant decomposition at default IDSC sensitivity settings. A study to determine the heat of fusion of DNNC using standard differential scanning calorimetry (DSC) at its 154.8 to 156.2 °C melting point revealed no significant DNNC sample decomposition.⁽⁵⁾ Permitting the melted DNNC sample to re-solidify, then conducting an IDSC liquid thermochemical decomposition at 176 °C gave virtually the same thermogram and heat of decomposition energy output as did a fresh DNNC sample under the same conditions. Conversely, the symmetrical, cyclic six-membered RDX nitramine and its eight-membered HMX homologue undergo a thermochemical decomposition during melting or liquefaction so rapidly that their heat of fusion cannot be determined.⁽⁵⁾

The thermochemical stability of solid state DNNC was investigated using the maximum IDSC instrument sensitivity settings several degrees below the DNNC melting point. Data obtained from these studies revealed that this compound undergoes a very slow but significant exothermic thermochemical decomposition process in the 142 to 148 °C temperature range following a three to five hour endothermic induction period. Using IDSC analyses of DNNC and its DNNC-d₆ perdeuterio-labeled analogue, the kinetic deuterium isotope effect (KDIE) approach was applied to this extended ambient pressure thermochemical decomposition to identify the rate-controlling bond rupture that governs the rate at which this solid state exothermic process proceeds and to determine the energy needed for its activation.

2 Experimental

The IDSC thermochemical decomposition curves were determined using a Perkin Elmer DSC 7 instrument and Perkin Elmer stainless steel large volume capsules (LVC), part no. 0319-1526 (top) and 0319-1525 (bottom) without Viton O-ring seals, part no. 0319-1535. DNNC and DNNC-d₆ sample sizes

ranging from 1.50 to 1.54 mg, were weighed into the LVC capsules and then sealed in the open atmosphere. During the IDSC thermochemical decomposition, the sealed capsules were under a stream of nitrogen gas using the highest sensitivity setting, following a contractor-accomplished instrumental calibration and fine tuning service call. The detailed synthesis procedure and characterization for the DNNC and DNNC-d₆ compounds have been reported.⁽⁶⁾ To ensure utmost accuracy, the DSC 7 temperature was calibrated with indium (mp 156.60 °C) prior to *each* IDSC sample run. A total of 32 IDSC runs were conducted. Six runs were conducted on DNNC at 148 °C and 145 °C, while five runs were conducted each on DNNC at 142 °C and DNNC-d₆ at 148 °C, 145 °C, and 142 °C.

The thermochemical decomposition curves for both DNNC and DNNC-d₆ were evaluated using the $d\alpha/dt = k\alpha(1-\alpha)$ autocatalytic rate plot where α is the mole fraction of decomposed DNNC at any given time (t).⁽⁷⁾ The α term is found as the Simpson's Rule area at any given time (t) interval defined as $\Delta\alpha/\Delta t$. Progressive summation of the Simpson's rule α areas provide the partial area (a) of decomposed DNNC under the IDSC curve after t minutes divided by the total area of decomposed DNNC under the entire IDSC curve, or $a = \text{summation of partial curve areas } (\alpha) \text{ at interval times } t / \text{total curve area}$, $a = \Sigma\alpha/A$.

IDSC measures the total heat evolved during the decomposition process, and because this heat evolution is proportional to the global rate at which the sample chemically reacts, the overall rate of decomposition is described by the following approximation: $d\alpha/dt = \text{height (h) of the IDSC curve above its baseline at time } t / \text{total area } A = h @ t/A$ because h is proportional to the very small $\Delta\alpha/\Delta t$ segment.⁽⁷⁾ This height-based approximation successfully has been used in the autocatalytic rate plots of IDSC curves where the thermochemical decomposition occurs over a period of minutes.^(8,9) However, the solid state DNNC and DNNC-d₆ thermochemical decomposition processes occurred over hour long durations (eg. nearly 14 hours at 145 °C). Since the IDSC instrumentation software can only plot a finite number of data points regardless of the total decomposition time, a longer decomposition process gives larger $\Delta\alpha/\Delta t$ values. Because of possibly large areas defined by the actual $\Delta\alpha/\Delta t$ areas, this height-based (h) approximation was not used. Rather, a more rigorous software program using a modification of the Simpson's Rule summation was written and developed to calculate the area of specific portions of the decomposed compound.

The standard Simpson's Rule divides equally distributed samples of a continuous curve into adjacent pairs of sub-intervals. Each pair of sub-intervals is defined by three data points: (1) the start of the first subinterval, (2) the end of the second subinterval, and (3) the point between them. Simpson's Rule uses these three points to create a polynomial curve that approximates the originally sampled decomposition curve. Consequently, the area under the polynomial curve also approximates the area under the originally sampled decomposition curve for the range specified by both sub-intervals. Using this approach, the area of a large portion of a sampled curve may be approximated by applying the Simpson's Rule to each adjacent pair of sub-intervals in that sample and aggregating the approximate area of each pair.

Simpson's Rule uses pairs of sub-intervals for $\Delta\alpha/\Delta t$ analysis which limits the flexibility of this approach, because it requires an even number of sub-intervals to be considered. To rectify this, Simpson's Rule was modified so that two sub-intervals were used to approximate the original decomposition curve as before, but only the area under the first sub-interval was approximated from this curve. Subsequent subintervals, such as the second one in the pair, were approximated in a similar fashion by pairing it with the next adjacent sub-interval. This modified approach also allows additional flexibility by making more individual $\Delta\alpha/\Delta t$ sub-intervals available in evaluating linear regression values. Such evaluation is used to determine optimum limits of linear portions in the autocatalytic rate

plot where a single coherent mechanistic kinetic step is occurring so that its associated rate constant (k) can be determined.

3 Results and Discussion

IDSC measurements taken with maximum instrument sensitivity at 142, 145, and 148 °C reveal that a very slow exothermic solid state DNNC thermochemical decomposition proceeds below its 155-156 °C melting point. This exothermic decomposition process appears after a three hour (184 min. at 148 °C) to nearly 5 hour (293 min. at 142 °C) endothermic induction period occurs. The exothermic thermochemical decomposition rate data from the IDSC analyses curves for DNNC and its DNNC- d_6 perdeuterio-labeled analogue show a positive kinetic deuterium isotope effect (KDIE). DNNC produces a distinctly slower exothermic decomposition when comparing the two superimposed DNNC and DNNC- d_6 IDSC curves taken at 148 °C (Figure 2).

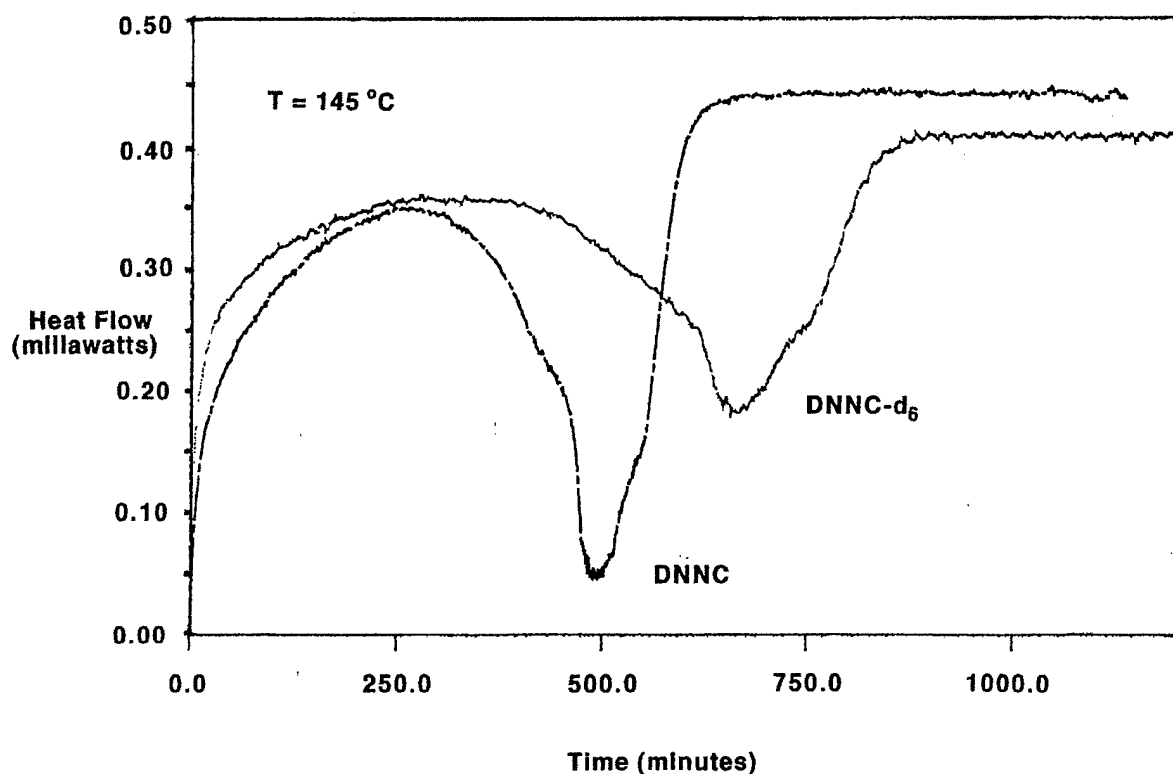


Figure 2. Real-time IDSC decomposition curve comparison of DNNC and DNNC- d_6 runs at 148 °C.

Rate data obtained from the IDSC curves and the magnitude of the KDIE rate constant ratio, k_h/k_d , suggest that carbon-hydrogen (C-H) bond rupture in one or both types of chemically unequivalent methylene groups of the DNNC molecule controls the rate of this exothermic thermochemical decomposition process.

Identification of the chemical bond rupture that controls the ambient pressure thermochemical decomposition rate process of both nitroaromatic and nitramine compounds has proved to be an important mechanistic feature which is mirrored in more drastic high pressure combustion and explosion

events.⁽¹⁰⁾ Indeed, it also appears this rate-controlling chemical bond rupture is a key mechanistic step in energetic compound global initiation and sensitivity properties.^(10,11)

The kinetic deuterium isotope effect (KDIE) has been used in conjunction with ambient pressure IDSC to identify the critical rate-controlling bond rupture that controls the thermochemical decomposition processes of liquid TNT (2,4,6-trinitrotoluene),⁽¹²⁾ and subsequently, solid TATB (1,3,5-triamino-2,4,6-trinitrobenzene),⁽⁸⁾ liquid and solid HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine),⁽⁹⁾ liquid RDX (1,3,5-trinitrohexahydro-1,3,5-triazine),⁽¹³⁾ and their respective deuterium-labeled TNT- α -d₃, TATB-d₆, HMX-d₈, RDX-d₆ analogues. Thermal gravimetric analysis (TGA)⁽¹⁴⁾ also has been used with HMX/HMX-d₈ and RDX/RDX-d₆ nitramines which produce mainly gaseous products during their liquid and solid state thermochemical decomposition processes.

In every case, the same rate-controlling bond rupture found in the ambient pressure thermochemical decomposition process for a given energetic compound^(8-10, 12-14) also appears to be the rate-controlling step for high pressure combustion^(15,16) and explosive initiation events.^(8, 17-22) With this fact in mind, the rate-controlling step in the solid-state thermochemical decomposition of DNNC and DNNC-d₆ was investigated by IDSC analysis using the KDIE approach.

3.1 Physicochemical Characteristics

IDSC measurements taken at maximum instrument sensitivity reveal that a very slow solid state DNNC thermochemical decomposition process occurs below its 155-156 °C melting point. IDSC analyses of DNNC taken at 142, 145, and 148 °C, following a three to nearly five hour endothermic induction period, produce an exothermic thermochemical decomposition curve whose autocatalytic rate plot displays three segments from which rate constant data can be obtained (Figure 3). The time required for the solid state decomposition process differs markedly from the liquid state process. For example, liquid state DNNC decomposition occurs at 176 °C over about 42 minutes (0.7 hours)⁽⁵⁾ while its entire solid state decomposition process at 145 °C requires nearly 14 hours or 20 times longer.

While the thermochemical stability, thermochemical decomposition rate, and explosive initiation sensitivity of DNNC more closely resemble those of TNT, the chemical reaction behavior of the solid state DNNC thermochemical decomposition process falls somewhere between that of its cyclic RDX or HMX nitramine relatives and the aromatic TNT compound. Over the extended solid state decomposition process, both DNNC and DNNC-d₆ lose an overall average of 75 percent sample mass to gaseous product formation and evolution (Table 1). Student t statistical analyses of the data in Table 1 confirm that all weight loss values are the same number at a 99.5 confidence correlation. This average weight loss, obtained for 32 sample runs, shows that the DNNC decomposition process, like that of RDX and HMX, predominantly generates small molecular weight gaseous products. There is, however, 25 percent of the original DNNC compound mass that remains as converted condensed phase byproduct(s). The HMX nitramine produces only gaseous decomposition products leaving no condensed phase material after complete decomposition,⁽⁹⁾ while TNT mainly produces condensed phase decomposition products.^(12, 23-25)

The presence of condensed decomposition products should instill some caution when assigning the bond rupture that controls the rate of a given thermochemical decomposition process. With condensed phase product formation, mechanistic consequences can be introduced that potentially dilute or reduce a true primary KDIE value below its accepted 1.35 experimental minimum to give an false secondary KDIE value in the 1.01 to 1.34 range.⁽¹²⁾

Table 1. Solid State DNNC and DNNC-d₆ Thermochemical Decomposition Mass Losses

Compound	Temperature (°C)	Mass Loss (%)	Standard Deviation
DNNC	148	78.5	± 5.1
DNNC-d ₆	148	74.7	± 1.8
DNNC	145	75.5	± 3.3
DNNC-d ₆	145	71.7	± 1.4
DNNC	142	75.2	± 1.5
DNNC-d ₆	142	<u>72.9</u>	± 1.3
		Ave. Mass Loss = 74.8 %	

3.1 Kinetic Results

The endothermic induction period (t_i) seen in Figure 3 can be evaluated for a kinetic deuterium isotope effect (KDIE) using a ratio of the DNNC-d₆ and DNNC induction times, t_{id}/t_{ih} . When this was first demonstrated with liquid TNT thermochemical decomposition,⁽¹²⁾ a primary KDIE of 1.66 was found. Further HPLC investigation coupled with this primary 1.66 KDIE value revealed a small concentration of catalytic species formed from the TNT itself by a rate controlling C-H bond rupture in the TNT pendant methyl group which required an activation energy equal to 194.6 kJ/mole. Upon reaching a threshold concentration, this catalytic species initiated the exothermic decomposition of TNT that showed an energy of activation equal to 123.0 kJ/mole.

Assuming that long temperature equilibration times do not occur during the induction time of the solid state DNNC sample, and that other non-kinetic crystal lattice or physicochemical factors are not present that might dilute or mask a true primary KDIE value, the t_{id}/t_{ih} induction period ratio reveals a KDIE equal to 1.21 (Table 2). Because assignment of the termination point for induction period of each decomposition curve often was no more accurate than ±10 minutes, the standard deviations at 148 and 145 °C can be treated as statistically significant. Should a small concentration of catalytic species be forming from DNNC, which then initiates the exothermic solid state decomposition, this secondary

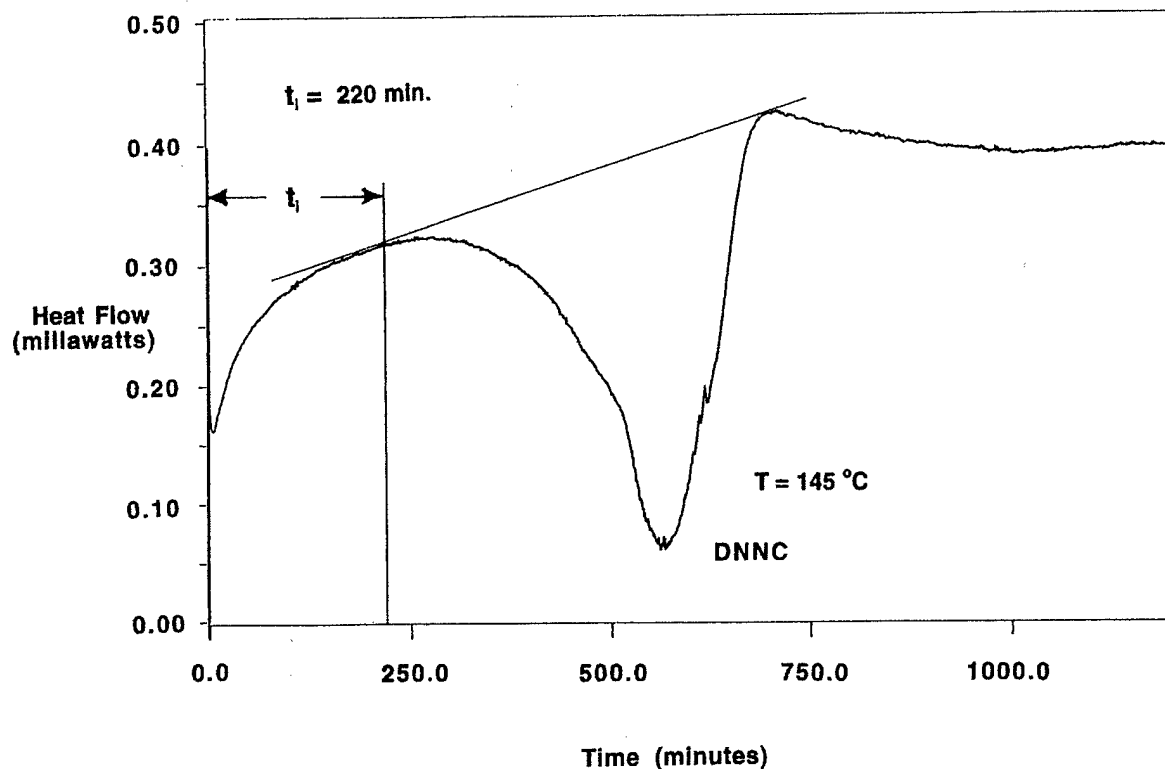


Figure 3. Induction period (t_i) analysis for a DNNC run at 145 °C.

KDIE value would suggest the rate-limiting step occurs either by pendant N-NO₂, ring C-N bond, or pendant C-NO₂ bond cleavage. Previous studies with the related RDX nitramine and larger HMX nitramine have addressed both possible N-NO₂ and ring C-N bond cleavage as possibly occurring in the decomposition process^(20-22, 26-32), but not during the rate-controlling step. Plotting $\ln t_i$ versus $1/T$ gives

DNNC INDUCTION PERIOD ACTIVATION ENERGY

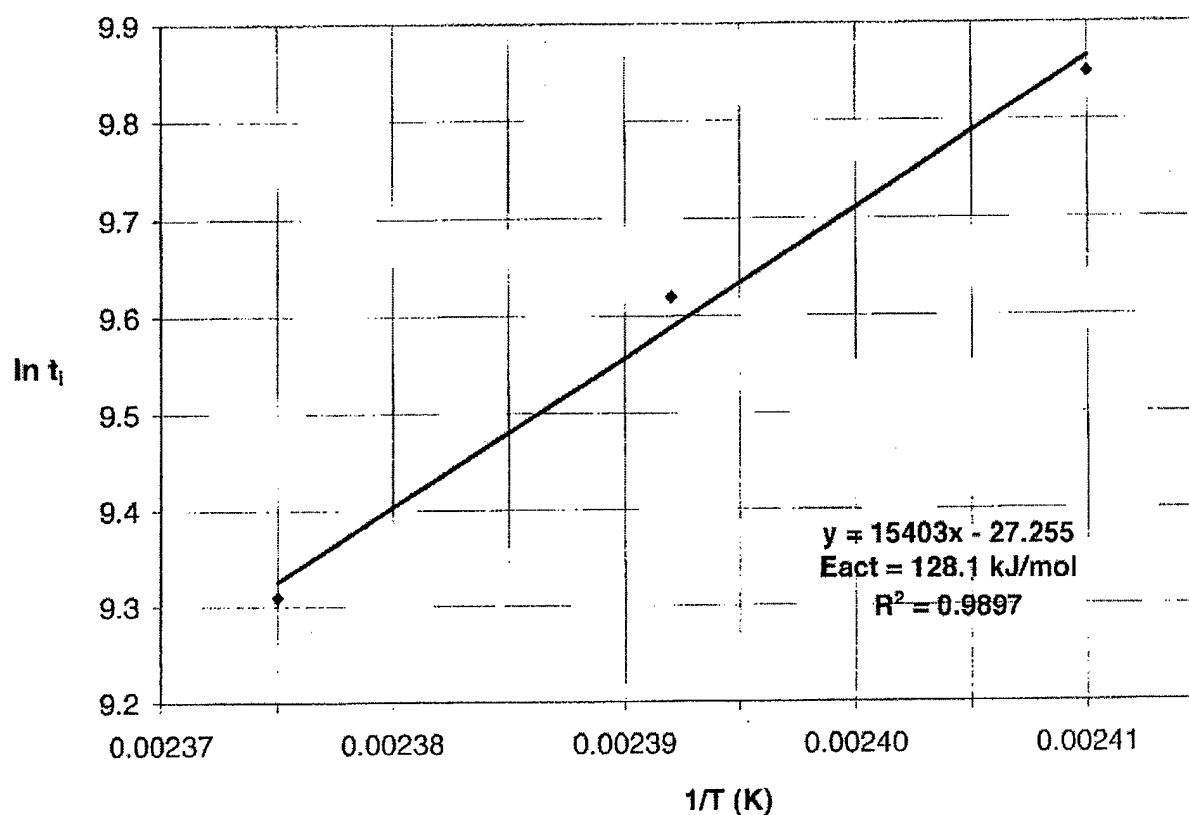


Figure 4. Energy of activation for induction period of DNNC decomposition curve from 142 to 148 °C.

a 128.1 kJ/mole activation energy for this DNNC induction period with a 0.990 linear regression data correlation which is significantly lower than the 194.6 kJ/mole energy of activation found during the induction period of the liquid state TNT thermochemical decomposition process.

Table 2. KDIE Data for Induction Period (t_i) Portion of the Thermochemical Decomposition Process

Compound	Temp. (°C)	t_i (min.)	Std. Dev.	KDIE
DNNC-d ₆	148	210	± 8	----
DNNC	148	184	± 18	1.14
DNNC-d ₆	145	316	± 31	----
DNNC	145	251	± 19	1.26
DNNC-d ₆	142	365	± 75	----
DNNC	142	293	± 67	<u>1.23</u>
				Overall KDIE = 1.21

Following the endothermic induction period, the exothermic decomposition is initiated. The autocatalytic rate plots obtained from these exothermic IDSC thermochemical decomposition curves reveal three linear segments for the DNNC and DNNC-d₆ at 145 and 148 °C (Figure 5). These linear segments occur in the early acceleratory portion [A], the later acceleratory portion [B], near the maximum heat energy release peak, and in the decay portion [C] of the decomposition curve. The slope of these three linear portions provide rate constant (k) data where an exothermic coherent, steady-state process is occurring during which one reaction pathway predominates in each.⁽⁹⁾ At the lowest 142 °C temperature, only early acceleratory [A] and decay portions [C] of the exothermic decomposition curve show linearity. Linearity in the later acceleratory portion [B] disappears. The percent of DNNC sample curve that undergoes thermochemical decomposition during these three linear segments combined is quite high, ranging from 66 to 62 percent for DNNC and 76 to 64 percent for DNNC-d₆ within the 142 to 148 °C temperature spread.

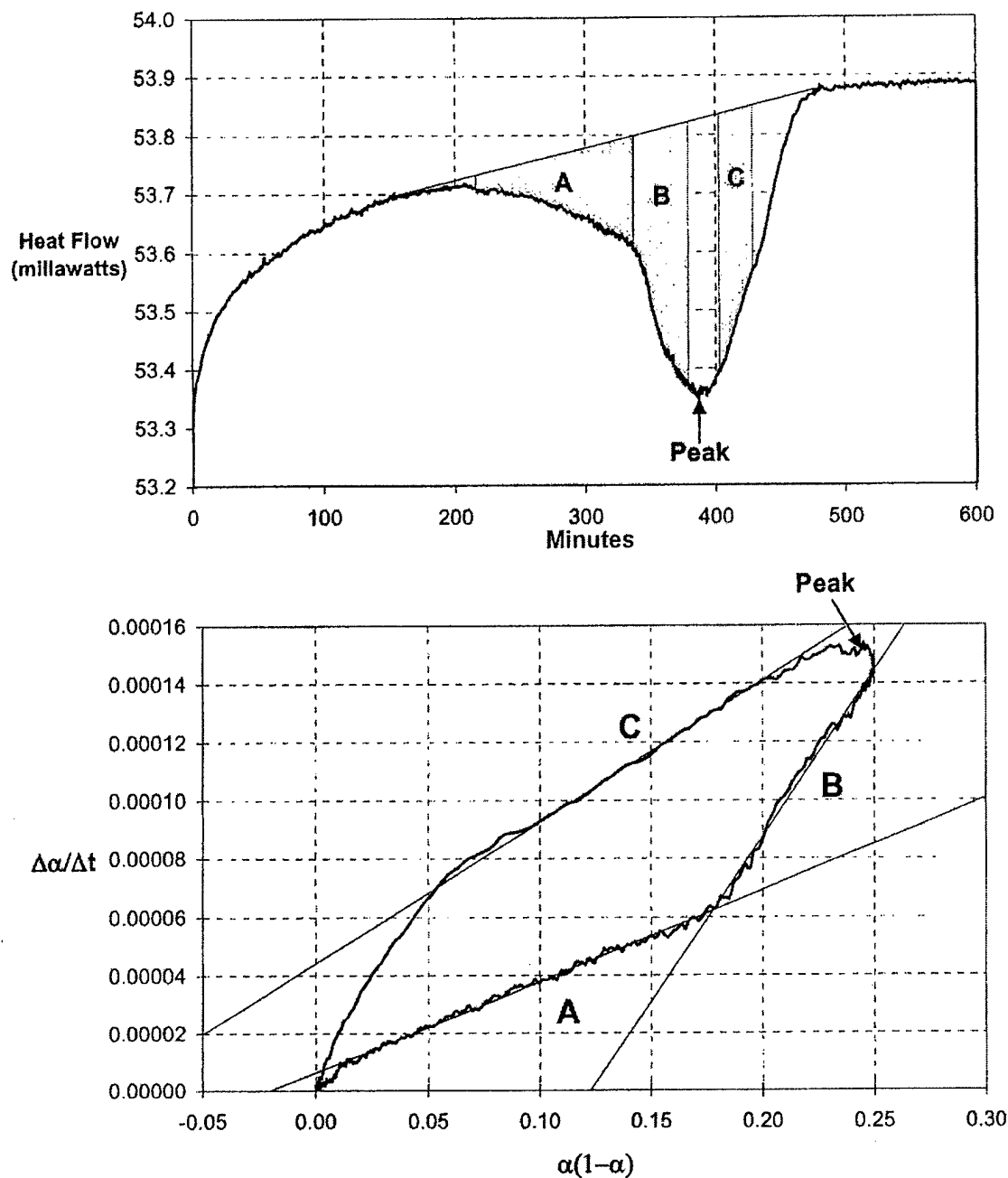


Figure 5. Comparison of DNNC IDSC decomposition curve (top) obtained at 148 °C and corresponding autocatalytic rate plot (bottom).

The linear segments of the autocatalytic rate plot generated from the exothermic solid state DNNC thermochemical decomposition curve can be compared with those seen with the HMX solid state decomposition process. Following a linear induction period, the HMX solid state thermochemical decomposition process produced two distinct linear segments in its autocatalytic rate plot. These linear segments occur during an acceleratory portion near the maximum energy release peak and later during its decay portion. The linear induction period, acceleratory portion, and decay portion of the HMX decomposition curve were found to reflect three different physical states, and each gave a different type

of KDIE, a primary, an inverse, and a secondary, respectively.⁽⁹⁾ While it has not been determined if the solid-state DNNC decomposition curve passes into another condensed physical state during its thermochemical decomposition process, all three linear segments (early acceleratory portion [A], later acceleratory portion [B], and decay portion [C]) of the DNNC autocatalytic rate plot produce a positive kinetic deuterium isotope effect (KDIE). The absence of an inverse KDIE with DNNC might suggest that DNNC remains in its solid state throughout the entire thermochemical decomposition process.

The extended 10 to 14 hour duration of the DNNC solid state thermochemical decomposition process, coupled with limitations on the total number of data points that the IDSC instrument can store, suggested that more accurate partial $\Delta\alpha/\Delta t$ curve area measurements, than previously used, might be necessary. A more rigorous increment-based autocatalytic rate plot program was developed, as described in the Experimental section, and was used to obtain the reaction rate constants, and subsequently, the KDIE values presented in this article.

Prior to developing this more rigorous increment-based autocatalytic rate program, several IDSC runs were evaluated using a formerly reported, height-based approximation for obtaining the $\Delta\alpha/\Delta t$ values needed to generate the autocatalytic rate plot for a given decomposition run.⁽⁷⁾ Although an approximation, the height-based autocatalytic rate constant values are surprisingly similar to those obtained using the increment-based autocatalytic rate program (Table 3).

Table 3. Height-Based vs. Increment-Based DNNC Autocatalytic Plot Rate Constants^(a) at 148 °C

Method	Early Acceleration [A]	Later Acceleration [B]	Decay Phase [C]
Height-Based	3.25 ± 0.23	9.06 ± 1.71	4.49 ± 0.45
Increment-Based	3.28 ± 0.25	8.94 ± 1.73	4.58 ± 0.48

(a) Rate constant values $\times 10^{-4} \text{ sec}^{-1}$.

\pm Data variations represent one standard deviation.

Table 4 illustrates the rigorous increment-based autocatalytic rate constant values obtained for the exothermic DNNC solid state thermochemical decomposition during its early acceleratory portion [A] at 142, 145, and 148 °C and for its analogous DNNC-d₆ compound. Particularly noteworthy are the exceptionally high linear regression correlation values for the DNNC and DNNC-d₆ autocatalytic rate plots. Such high linear regression correlation values are somewhat unusual in IDSC decomposition kinetic rate plots.

Table 4. Kinetic Data for Early Acceleratory Portion [A] of the Thermochemical Decomposition Process

Compound	Temp. (°C)	$k \times 10^{-4} \text{ (s}^{-1}\text{)}$	Std. Dev. $\times 10^{-4}$	KDIE	R^2
DNNC	148	3.38	± 0.24	-----	0.998
DNNC-d ₆	148	2.51	± 0.16	1.35	0.994
DNNC	145	3.13	± 0.36	-----	0.997
DNNC-d ₆	145	2.02	± 0.14	1.55	0.995
DNNC	142	2.36	± 0.10	-----	0.998
DNNC-d ₆	142	1.56	± 0.26	<u>1.51</u>	0.995
Overall KDIE = 1.47					

R^2 = Linear correlation fit to early acceleratory portion of the autocatalytic rate plot.

The early acceleratory portion [A] of the exothermic solid state DNNC decomposition reveals an average KDIE equal to 1.47 in the 142 to 148 °C temperature range and strongly suggests a primary KDIE. This KDIE value was obtained from autocatalytic rate plots that gave very impressive overall 0.998 (DNNC) and 0.994 (DNNC-d₆) linear regression correlation factors (R^2). This early acceleratory portion [A] constitutes 16 to 17 percent of the total decomposition curve at 148 and 145 °C respectively, but noticeably increases to 38% at 142 °C (Table 5).

The primary 1.47 KDIE value in [A] suggests that C-H bond rupture, in the either one type or both types of chemically inequivalent DNNC ring methylene groups, constitutes the rate-controlling step for its exothermic solid-state thermochemical decomposition. This 1.47 KDIE value exceeds the theoretical high temperature lower limit of 1.41 and the experimentally accepted 1.35 lower limit for a primary KDIE.^(9, 10a, 12-13) Assignment of a primary KDIE further is supported by a mathematically normalized KDIE value of 2.52 at standard 298 K (25 °C) temperature calculated from the experimental 1.47 KDIE value using an average decomposition temperature of 145 °C.⁽³³⁾ At 25 °C, a 2.5 value constitutes the accepted minimum threshold for a primary KDIE.⁽³⁴⁾

Table 5. Percent of IDSC Decomposition Curve covered by the Linear Early Acceleratory Portion [A]

Compound	Temperature (°C)	% Decomposition	Std. Deviation	R ²
DNNC	148	16.7	± 7.9	0.998
DNNC-d ₆	148	16.2	± 5.6	0.994
DNNC	145	18.2	± 6.3	0.997
DNNC-d ₆	145	26.9	± 5.1	0.995
DNNC	142	37.6	± 3.1	0.998
DNNC-d ₆	142	39.5	± 4.9	0.994

R² = Linear correlation fit to early acceleratory portion of the autocatalytic rate plot.

The latter acceleratory portion [B] of the solid-state DNNC and DNNC-d₆ autocatalytic rate curves near the exothermic maximum peak (Figure 5) gives an average primary KDIE value of 1.64 at 148 °C and 145 °C. The linear segment of the autocatalytic rate plot covers 22 to 26 percent of the total decomposition curve at the 148 °C, decreases to 10 to 14 percent at 145 °C, and disappears at 142 °C. This linear segment also reveals a very unusual characteristic or artifact which could indicate the decomposition process is influenced by some factor other than purely normal kinetics. Table 6 illustrates the “apparent” kinetics data obtained at 148 °C and 145 °C for this latter acceleratory portion [B]. With both the DNNC and DNNC-d₆ compounds, the rate constant present at 148 °C very

Table 6. Kinetic Data for Later Acceleratory Portion [B] of the Thermochemical Decomposition Process

Compound	Temp. (°C)	k x 10 ⁻⁴ (s ⁻¹)	Std. Dev. x 10 ⁻⁴	KDIE	R ²
DNNC	148	8.70	± 0.36	-----	0.997
DNNC-d ₆	148	5.45	± 0.95	1.60	0.997
DNNC	145	14.74	± 0.47	-----	0.994
DNNC-d ₆	145	8.74	± 0.34	<u>1.69</u>	0.984
Overall KDIE = 1.64					

R² = Linear correlation fit to early acceleratory portion of the autocatalytic rate plot.

surprisingly increases at the lower 145 °C temperature. We have no current explanation for this unexpected result. If one assumes this unexplained characteristic contributes equally for both DNNC and DNNC-d₆ in affecting the unexpected rate constant increase, the KDIE of 1.64 again could suggest a rate-limiting C-H bond rupture. As discussed earlier, a similar segment of the autocatalytic rate plot for

solid state HMX thermochemical decomposition gave instead, an inverse KDIE which suggested HMX converted into a mixed melt transition from its solid to its liquid state.⁽⁹⁾ Unlike HMX, the 1.64 primary KDIE value for the DNNC latter acceleratory portion [B] may suggest its solid state crystal lattice is not undergoing the same crystal lattice disruption into a liquid state conversion.

The decay portion [C] of the DNNC thermochemical decomposition affords a 1.27 KDIE value over the 148 to 142 °C temperature range (Table 7). The linear segment of the autocatalytic rate plot covers 22 to 34 percent of the total decomposition curve for DNNC and a similar 26 to 34 percent for DNNC-d₆. By magnitude alone, this 1.27 value might suggest a secondary KDIE and a resultant change in the rate-controlling mechanistic step. A secondary KDIE value would fall in a 1.01 to 1.34 experimental range. This is the case for the HMX nitramine, where the rate-controlling C-H bond rupture defined the rate controlling solid state decomposition, then transitions to a rate-controlling ring C-N bond cleavage in its liquid state.⁽⁹⁾ HMX, however, converts entirely to product gases and leaves no condensed phase

Table 7. Kinetic Data of the Decay Portion [C] of the Thermochemical Decomposition Process

Compound	Temp. (°C)	k x 10 ⁻⁴ (s ⁻¹)	Std. Dev. x 10 ⁻⁴	KDIE	R ²
DNNC	148	4.36	± 0.52	-----	0.996
DNNC-d ₆	148	3.52	± 0.65	1.24	0.992
DNNC	145	3.13	± 0.32	-----	0.988
DNNC-d ₆	145	2.78	± 0.78	1.13	0.973
DNNC	142	2.19	± 0.46	-----	0.976
DNNC-d ₆	142	1.53	± 0.36	<u>1.43</u>	0.970
				Overall KDIE = 1.27	

R² = Linear correlation fit to early acceleratory portion of the autocatalytic rate plot.

byproduct(s) during its decomposition process. While an average 75 percent of the exothermic DNNC decomposition products are small gaseous molecules, the average 25 percent condensed phase byproduct(s) in the 148 °C and 142 °C temperature range introduces the possibility that the true KDIE value for DNNC is being reduced or diluted from its true value during this late decomposition stage [C]. A reduced or diluted primary KDIE can result from further decomposition of condensed phase byproduct(s) whose mechanistic pathway or chemical structure do not involve, nor permit, a rate-limiting C-H bond rupture. Such a dilution of a primary KDIE value has been documented in the decay portion of the liquid TNT⁽¹²⁾ and solid TATB^(8, 10a,b, 19) decomposition processes where condensed byproducts form.²² Secondly, KDIE thermochemical decomposition studies conducted specifically on liquid DNNC and DNNC-d₆ show no evidence of a secondary KDIE.⁽³⁵⁾ This fact further suggests the 1.27 KDIE value for the DNNC decay portion is not a true secondary KDIE and further indicates that DNNC probably does not transition into the liquid state during the latter acceleratory portion [B] of its decomposition process.

Past mechanistic IDSC-based KDIE thermochemical decomposition studies of liquid state TNT,⁽¹²⁾ solid state TATB,⁽⁸⁾ solid state HMX,⁽⁹⁾ and liquid state RDX⁽¹³⁾ clearly reflect the mechanistic importance that the early portion of the thermochemical decomposition curve contributes to the overall

decomposition process. KDIE values obtained either during an induction period, or from linear first order or autocatalytic rate plots occurring in during the early acceleratory phase, can reveal the key mechanistic rate-controlling step that determines the overall decomposition rate. This occurs because these regions are least affected by additional complicating factors that can be generated and that can appear during the latter stages of the decomposition process.

Accordingly, the possible formation of a catalytic species from the DNNC itself, by either pendant N-NO₂, ring C-N or pendant C-NO₂ bond rupture, could be the rate controlling step for initiating the solid state DNNC exothermic thermochemical decomposition. The primary KDIE equal to 1.47, found during DNNC during the early exothermic acceleratory portion [A], likely defines C-H bond rupture as being the rate-controlling step once exothermic decomposition is initiated.

The energy of activation was determined for this exothermic DNNC-d₆ solid state thermochemical decomposition portion [A] by plotting its respective rate constant logarithm against each corresponding reciprocal temperature. Figure 6 reveals a 115.2 kJ/mole activation energy for DNNC-d₆ with an exceptional 0.998 linear regression correlation. If the rate-controlling methylene C-H bond rupture occurs during the activation step, a lower energy of activation for unlabeled DNNC should result.

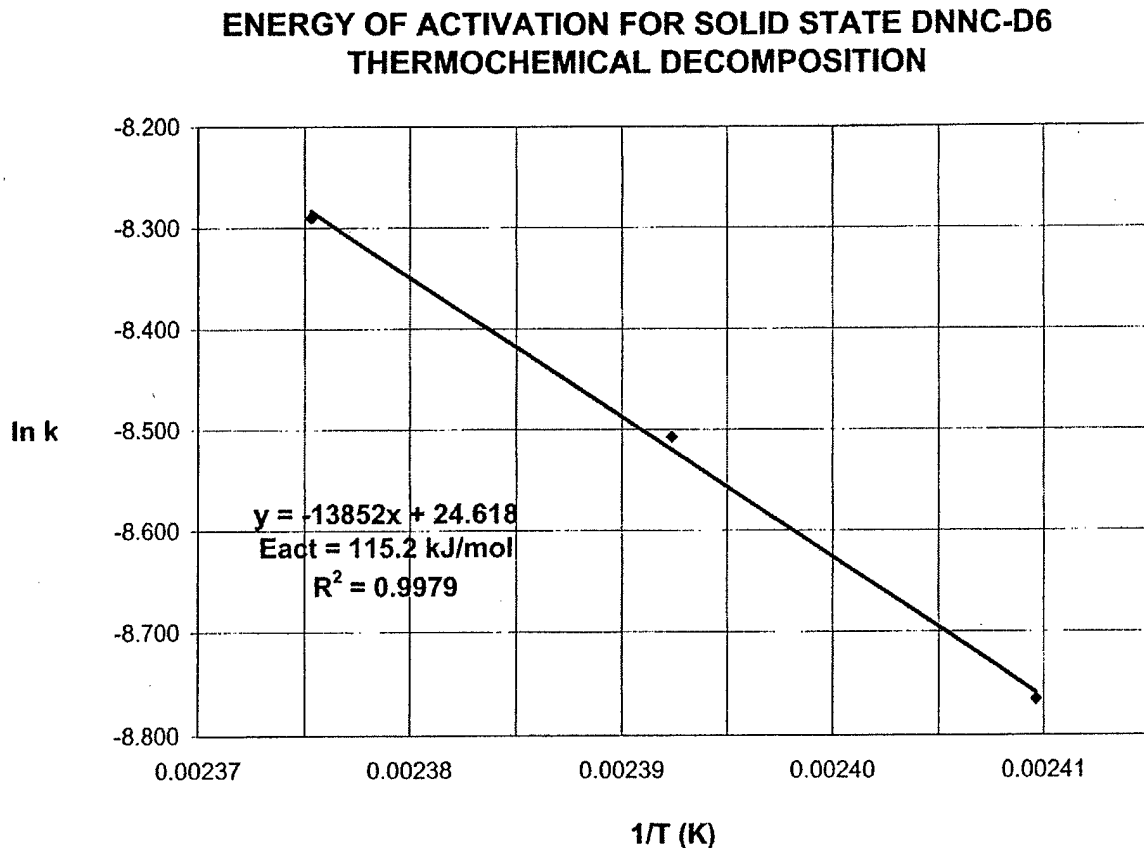


Figure 6. Energy of activation for early exothermic acceleratory portion [A] of DNNC-d₆ decomposition curve from 142 to 148 °C.

Because the ground state zero vibrational energy difference between the C-H and the stronger C-D bond is 9.6 kJ/mole (2.3 kcal/mole), the DNNC activation energy then might be expected to be 9.6 kJ/mole less than that of DNNC-d₆ or close to 105.6 kJ/mole. An analogous energy of activation plot to Figure 5

for DNNC gave an activation energy equal to 87.1 kJ/mole, but with only a 0.904 linear regression correlation. Considering this low linear regression correlation, the DNNC 105.6 kJ/mole energy of activation calculated from the DNNC-d₆ data might be the more reasonable value. This 105.6 kJ/mol value, being about 22 KJ/mole lower than the 128.1 kJ/mole activation energy of the induction period, might further suggest that a small threshold concentration of catalytic species forms during the endothermic induction period that initiates the exothermic acceleratory decomposition. If this is so, it forms by a different rate-limiting step than the C-H bond rupture that controls the energy release rate during the exothermic DNNC thermochemical decomposition [A].

4 Conclusions

Previously reported mechanistic KDIE-based thermochemical decomposition investigations of liquid state TNT/TNT- α -d₃, solid state TATB/TATB-d₆, solid state HMX/HMX-d₈, and liquid state RDX/RDX-d₆ by isothermal DSC (IDSC) analysis clearly show the importance the early portion the thermochemical decomposition process exerts in determining the specific chemical bond rupture that controls the decomposition process and its associated energy release rate. With this in mind, the solid state decomposition of DNNC and perdeuterio DNNC-d₆ analogue were investigated by IDSC.

Data obtained from the decomposition curves show that DNNC likely remains in its solid state during the entire decomposition process within the 142 °C to 148 °C temperature range investigated. An apparent secondary 1.21 KDIE value occurs during the initial endothermic induction period. This could indicate formation of a catalytic species by a rate-limiting pendant N-NO₂, ring C-N, or pendant C-NO₂ bond cleavage, which upon reaching a small threshold concentration, initiates its subsequent exothermic energy release. A 128.1 kJ/mole activation energy is found for the induction period.

Analysis of the exothermic energy release during the early acceleratory portion [A] of the DNNC decomposition curve shows a 1.47 KDIE value. The 1.47 KDIE value suggests that C-H bond rupture in one or both types of chemically inequivalent ring methylene groups constitutes the rate-controlling mechanistic step for the energy release rate of the DNNC molecule. Once the exothermic solid state DNNC decomposition is initiated, C-H bond cleavage likely predominates as the exothermic rate-controlling step throughout the remaining thermochemical decomposition process. An activation energy equal to 105.6 kJ/mol for the early exothermic acceleratory portion [A] is calculated from a measured 115.2 kJ/mol activation energy for the DNNC-d₆ early exothermic acceleratory portion. The lower 105.6 kJ/mol activation energy, when compared with higher the 128.1 kJ/mol induction period activation energy, further supports the possible induction period formation of a catalytic species from DNNC itself.

5 References

- (1) (a) Present address: School of Information and Computer Science, University of California, Irvine, Irvine CA 92697 (USA).
(b) Experimental IDSC thermochemical decomposition investigations were conducted at The F. J. Seiler Research Laboratory, USAF Academy, CO (USA) prior to its Sep 30, 1995 decommissioning.
(c) Adjunct Professor, Pt. Loma Nazarene University, San Diego, CA, Aug 1997 to Aug 2003.
- (2) D. L. Levins, C. D. Bedford, and C. L. Coon, U.S. Patent 4,346,222, **1982**, SRI International, USA.
- (3) D. A. Cichra and H. G. Adolph, Nitrolysis of Dialkyl tert-Butylamines, *J. Org. Chem.* **1982**, 47, 2472-2476.

- (4) J. Boileau, M. Piteau, and G. Jacob, Synthese de la 1,3,5,5-tetranitrohexahydropyrimidine, *Propellants, Explos. Pyrotech.* **1990**, *15*, 38. The subject DNNC compound also has appeared in the literature under the acronym of TNDA.
- (5) S. A. Shackelford and J. F. Goldman, Heat of Fusion for 1,3,5,5-Tetranitrohexahydropyrimidine (DNNC) and its DNNC-d₆ Deuterium Labelled Analogue, *Propellants, Explos., Pyrotech.* **1995**, *20*, 1-4, and references cited therein.
- (6) S. A. Shackelford, Synthesis of 1,3,5,7-Tetranitrohexahydropyrimidine-2,2,4,4,6,6-d₆ (DNNC-d₆) and Its Adiol-d₄ Precursor Using Paraformaldehyde-d₂ and Unlabeled Reaction Ingredients, *J. Labeled Compds. and Radiopharm.* **1991**, *XXIX*, 1197-1206.
- (7) R. N. Rogers, *Quantitative Evaluation of Thermal Hazards*, RCEM Report A-04-87, November 4, **1987**, pp. 15-65, Research Center for Energetic Materials, New Mexico Tech., Socorro, NM, USA 87081.
- (8) R. N. Rogers, J. L. Janney, M. H. Ebinger, Kinetic Isotope Effects in Thermal Explosions, *Thermochim. Acta* **1982**, *59*, 287-298.
- (9) S. A. Shackelford, M. B. Coolidge, B. B. Goshgarian, B. A. Loving, R. N. Rogers, J. L. Janney, M. H. Ebinger, Deuterium Isotope Effects in Condensed-Phase Thermochemical Decomposition Reactions of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Phys. Chem.* **1985**, *89*, 3118-3126.
- (10) S. A. Shackelford, J. W. Beckmann, J. S. Wilkes, Deuterium Isotope Effects in the Thermochemical Decomposition of Liquid 2,4,6-Trinitrotoluene: Application to Mechanistic Studies Using Isothermal Differential Scanning Calorimetry Analysis, *J. Org. Chem.* **1977**, *42*, 4201-4206.
- (11) L. A. Wiseman, *Bristol Research Ret. No. 51*, A. C. 2670, Ministry of Supply, Great Britain, **1942**.
- (12) R. N. Rogers, Combined Pyrolysis and Thin Layer Chromatography: A Method for the Study of Decomposition Mechanisms, *Anal. Chem.* **1967**, *39*, 730-733.
- (13) J. C. Dacons, H. G. Adolph, M. J. Kamlet, Some Novel Observations Concerning the Thermal Decomposition of 2,4,6-Trinitrotoluene, *J. Phys. Chem.* **1970**, *74*, 3035-3040.
- (14) (a) S. A. Shackelford, Mechanistic Investigations of Condensed Phase Energetic Material Decomposition Processes Using the Kinetic Deuterium Isotope Effect, in S. N. Bulusu (Ed.) *Chemistry and Physics of Energetic Materials*, NATO ASI Series, Series C, Vol 309, Kluwer Academic Press, Dordrecht, The Netherlands, **1990**, pp. 413-432 (Chapter 18).
 (b) S. A. Shackelford, Mechanistic Relationships of the Decomposition Process to Combustion and Explosion Events From Kinetic Deuterium Isotope Effect Investigations, in S. N. Bulusu (Ed.) *Chemistry and Physics of Energetic Materials*, NATO ASI Series, Series C, Vol 309, Kluwer Academic Press, Dordrecht, The Netherlands, **1990**, pp. 433-456 (Chapter 19) and references cited therein.
- (15) S. A. Shackelford, A General Concept Concerning Energetic Material Sensitivity and Initiation, *J. de Physique IV*, [Colloque C4, supplement au *J. de Physique III* **1995**, *5*, 485-499,].
- (16) S. L. Rodgers, M. B. Coolidge, W. J. Lauderdale, S. A. Shackelford, Comparative Mechanistic Thermochemical Decomposition Analyses of Liquid Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) Using the Kinetic Deuterium Isotope Effect Approach, *Thermochim. Acta* **1991**, *177*, 151-168.
- (17) S. N. Bulusu, D. J. Weinstein, J. R. Autera, R. W. Velicky, Deuterium Kinetic Isotope Effect in the Thermal Decomposition of 1,3,5-Trinitro-1,3,5-triazacyclohexane and 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane: Its Use as an Experimental Probe for Their Shock-Induced Chemistry, *J. Phys. Chem.* **1986**, *90*, 4121-4126.
- (18) S. A. Shackelford, B. B. Goshgarian, R. D. Chapman, R. E. Askins, D. A. Flanagan, R. N. Rogers, Deuterium Isotope Effects During HMX Combustion: Chemical Kinetic Burn Rate Control Mechanism Verified, *Propellants, Explos. Pyrotech.* **1989**, *14*, 93-102.

- (18) S. A. Shackelford, B. B. Goshgarian, R. D. Chapman, R. E. Askins, D. A. Flanigan, R. N. Rogers, Deuterium Isotope Effects During HMX Combustion: Chemical Kinetic Burn Rate Control Mechanism Verified, *Propellants, Explos. Pyrotech.* **1989**, *14*, 93-102.
- (19) S. A. Shackelford, S. L. Rodgers, R. E. Askins, Deuterium Isotope Effects During RDX Combustion: Mechanistic Rate-Controlling Step Determination, *Propellants, Explos. Pyrotech.* **1991**, *16*, 279-286.
- (20) S. N. Bulusu, J. R. Autera, Initiation Mechanism of TNT: Deuterium Isotope Effect as an Experimental Probe, *J. Energetic Matls.* **1983**, *1*, 133-140.
- (21) J. Sharma, W. L. Garrett, F. J. Owens, V. L. Vogel, X-Ray Photoelectron Study of 1,3,5-Triamino-2,4,6-trinitrobenzene, *J. Phys. Chem.* **1982**, *86*, 1657-1661.
- (22) J. Sharma, J. C. Hoffsommer, D. J. Glover, C. S. Coffey, F. Santiago, A. Stolovy, S. Yasuda, Comparative Study of Molecular Fragmentation in Sub-Initiated TATB Caused by Impact, UV, Heat, and Electron Beams, in J. R. Asay, R. A. Graham, G. K. Straub (Eds.) *Shock Waves in Condensed Matter*, Elsevier, **1984**, pp. 543-546.
- (23) J. Sharma, J. C. Hoffsommer, D. J. Glover, C. S. Coffey, J. W. Forbes, T. P. Liddiard, W. L. Elban, F. Santiago, Sub-Ignition Reactions at Molecular Levels in Explosives Subjected to Impact and Underwater Shock, *8th International Symposium on Detonation*, Albuquerque, 15-19 July **1985**.
- (24) J. Sharma, J. W. Forbes, C. S. Coffey, T. P. Liddiard, The Physical and Chemical Nature of Sensitization Centers Left from Hot Spots Caused in Triaminotrinitrobenzene by Shock and Impact, *J. Phys. Chem.* **1987**, *91*, 5139-5144.
- (25) J. Sharma, J. W. Forbes, C. S. Coffey, T. P. Liddiard, The Nature of Reaction Sites and Sensitization Centers in TATB and TNT, in S. C. Schmidt, N. C. Holmes (Eds.), *Shock Waves in Condensed Matter*, Elsevier, **1988**, pp. 565-568.
- (26) J. D. Cosgrove, A. J. Owen, The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-triazine (RDX) - Part II: The Effects of the Products, *Comb. Flame* **1974**, *22*, 19-22.
- (27) M. A. Schroeder, Critical Analysis of Nitramine Decomposition Results: Some Comments on Chemical Mechanism, In *Proceedings of the 16th JANNAF Combustion Meeting*, Monterey, CA, Chemical Propulsion Information Agency, The Johns Hopkins Univ., Laurel, MD, CPIA Publ. No. 308, **1979**, Vol. II, pp. 17-34;
- (28) M. D. Pace, A. D. Britt, W. B. Moniz, EPR Investigations of Thermal Decomposition of Nitramines: I. Primary Nitroxide Radicals from RDX, *J. Energetic Matls.*, **1983**, *1*, 141-175.
- (29) R. A. Fifer, Chemistry of Ester and Nitramine Propellants, In K. K. Kuo, M. Summerfield (Eds.), *Fundamentals of Solid Propellant Combustion*, of Progress in Astronautics and Aeronautics, **1984**, Vol 90, AIAA, Inc., pp. 178-237.
- (30) R. Shaw, F. E. Walker, Estimated Kinetics and Thermochemistry of Some Initial Unimolecular Reactions in the Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane in the Gas Phase, *J. Phys. Chem.*, **1977**, *81*, 2572-2576.
- (31) J. Kimura, N. Kubota, "Thermal Decomposition Process of HMX", *Prop. Explos.*, **1980**, *5*, 1-8.
- (32) A. D. Britt, M. D. Pace, W. B. Monitz, EPR Investigations of Thermal Decomposition of Nitramines: II. Primary Nitroxide Radicals from HMX, *J. Energetic Matls.*, **1983**, *1*, 367-371.
- (33) T. H. Lowery, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, 2nd Ed., New York, **1981**, pp. 206-207.
- (34) G. W. Klump, *Reactivity in Organic Chemistry*, L. Birladeanu, (Transl.), Wiley Interscience, New York, **1982**, p. 262.

- (35) (a) S. A. Shackelford, J. F. Goldman, Intramolecular Mechanistic Thermochemical Decomposition Studies of 1,3,5,5-Tetranitrohexahydropyrimidine and Its Deuterium Labeled Analogues, 203rd *National American Chemical Society Meeting*, San Francisco, CA, 5-10 April 1992;
(b) S. A. Shackelford, J. F. Goldman, Influence of Chemical Structure on the Rate-Controlling-Step of DNNC (TNDA) Decomposition Kinetics, 22nd *Int. Annual Conference of ICT*, Karlsruhe, Germany, July 2-5, 1991.

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